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PHENOL IN RELATIONSHIP TO TASTE AND ODOR PROBLEMS

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Cincinnati, Ohio

1958

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U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
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Consideration of water quality requirements must ultimately be based on satisfying the needs and requirements of the average home consumer. If he lives in a single family house, his daily home water usage is approximately as follows:(1)

Toilet flushing	25 gallons
Bathing and personal cleanliness	25 gallons
Laundry usage	15 gallons
Kitchen usage	10 gallons

Critical requirements for the taste and/or odor of water arise in relation to two types of water usage:

1. Water used for personal cleanliness.
2. Water used for drinking and culinary purposes.

The consumer is likely to be quite exacting in judging the odor of water he uses for personal hygiene. He surrounds himself with a fine spray of hot water if he takes a shower. If he uses a tub he enters a small space and splashes around in a large vat of hot water. A frequent complaint about water quality I have heard relates to the odor of water in the shower.

Let's look at the shower a little closer. Before the water gets there a lot of it goes through a hot water heater. In the heater, the water

is heated to perhaps 140°F. It may be held for over 48 hours before use in an electric water heater such as I have. If the water is heated with gas, it frequently stays in the heater for over 12 hours. These retention periods are enough to develop odors which otherwise would not be present in high concentration in water containing ingredients such as chloramines and phenols which can react to yield odor.

Most of the water the consumer uses in the kitchen goes for washing dishes, cleaning vegetables, etc. The adult consumer is likely to drink about one-half gallon or less of water. He takes in much of his daily fluid requirements in the form of coffee.

Coffee made in a percolator is made with boiling water. Heat accentuates the odors in the water. If there are potentially reactive chemical ingredients, the heat will hasten reactions. Perhaps, some of the poor coffee you have had represents water that developed taste and odor when it was heated in the brewing process.

In considering the way odor affects the consumer, it is necessary to consider whether his senses make addition of the odors of different materials.

Assuming that chemical reactions are not involved, the answer to the question above lies in the determination of whether odor stimuli by unrelated individual materials are additive and/or synergistic or whether they are non-additive and/or antagonistic. If it be assumed that the threshold concentration of material A is "a" and the threshold concentration of material B is "b" then the question is posed by the statement:

$$\frac{a}{2} + \frac{b}{2} \gtrless TOC$$

where TOC is the threshold odor concentration.

This question has been given some study in the SEC laboratories by A. A. Rosen. So far he has measured human response to odor stimuli by combinations of two and three specific chemicals at a time, but only a limited number of chemicals have been investigated. To date his findings give the answer.

$$\frac{a}{2} + \frac{b}{2} \geq \text{TOC}$$

There is little reason to believe that this finding will not hold up in most circumstances and it represents the best basis presently available for considering the questions involved. In words, the mathematical notations say that human sensory response to individual odorous chemicals in a mixture is at least additive and that it may be greater than additive response. This says further that there is no unimportant contribution to total odor.

We have previously stated(2) that there is no odor for water that the public is likely to accept without long conditioning. All of you know very well that the public doesn't want water that smells like bananas, bourbon, or peppermint. This is a point we need not belabor.

But what determines odor quality? Unpublished data collected by Setter and whitfield at SEC indicated that odor quality could be changed by material responsible for less than one-half of the total odor present with the rest of the odor due to a single well defined chemical.

If I enter the house when my wife is baking a cake I can tell this immediately by the smell. And it smells like a cake baking. The dominant odor may be extract of vanilla, and if I am clever I can recognize this component of the odor. Above this, the dominant odor will be vanillin. The chances are it would smell like a cake to most of you also. Clearly

your everyday experience with cake or beef stew tells you that odors add up and that a material may be responsible for a substantial portion of total odor without determining your picture of what causes the odor. This conclusion checks common experience. We would be most uneasy if we found that an onion and a pepper had no more odor together than the onion had alone.

The variability of the senses of the consumer and the relationship of this variability to water quality requirements and water quality measurement have already been discussed at some length(3). On most odors, the most sensitive 5 per cent of the population is estimated to be from 2 to 10 times as sensitive as the average man. The man with keener senses than his fellows is obviously going to be harder to please in terms of water taste and odor. It is not unreasonable to try to make water suitable for drinking by whole populations, and water quality is certainly poor when 50 per cent or even 25 per cent of the consuming population find the water unpalatable.

Summing up, the taste and odor of water should be acceptable to at least 95 per cent of the using population, regardless of whether the water is newly pumped from the treatment plant or has been hung up in a reservoir en route. The water should not develop tastes and odors when it is heated and held in the consumer's hot water heater, or when he heats it up to make his coffee.

Some Pollutional Characteristics of Phenol

Ettinger and Ruchhoft(4) described the destruction of phenol and cresols added to surface waters and studied factors governing behavior of

these materials therein. Biological oxidation was found to be the principal cause of the destruction. Under favorable conditions, phenol destruction was complete in a relatively brief period. At least six factors affected the metabolic rates of the organisms destroying the phenolic materials; temperature, metabolic lag, the nature of the initial microbiological population of the water, the concentration of the phenolic compound, the specific compound involved, and the presence of nutrients such as nitrogen and phosphorus to permit utilization of the phenolic material in microbiological metabolism.

In general the Mahoning River usually meets many of the criteria of conditions required for optimum rates of phenol assimilation. The Mahoning River, as noted by the Ohio River survey[5], and presently reaffirmed by Kinney, requires a combination of cold weather and increased runoff to move substantial amounts of phenol downstream.

Phenols as an Indicator of Unsatisfactory Water Quality

Phenols may be regarded as an indicator of sorts. Normally, they do not occur in raw water in any substantial amount unless the water is polluted by phenolic wastes in the immediate vicinity or conditions are favorable for the travel of pollutants which undergo self-purification readily. Phenols do not travel efficiently in streams but they usually occur along with a great deal of other and frequently more persistent organic pollutants. Further, phenols usually occur in highly industrialized areas where pollution from other sources also enters the river. Phenols may be regarded as both a direct impairment of water quality and an indicator that stream self-purification processes are inadequate to protect

water supplies from other chemicals entering the stream with them or in their general vicinity. Clearly, the presence of phenols in a water is a strong demonstration that there is not adequate stream purification to give good reduction in pollution between the water plant and the phenol source.

One should not be surprised to find correlation between phenol content in raw waters and severe problems of water quality. However, it does not follow that water quality problems will show major improvement simply as the result of reduction or removal or phenolic contamination, even though the phenolic pollution constitutes a well defined water quality impairment. In practice, it is difficult to remove phenols without affording some relief from pollution by other chemicals which accompany them. We have never heard of a water supply that showed a lot of phenol but was otherwise of good quality.

Recent work by Burttschell, et al[6] at the Sanitary Engineering Center has done much to chart the pathway of reaction in the production of taste and odor in the course of the chlorination of phenol. It was found that when phenol is chlorinated it yields the normal chlorination products predictable from the general knowledge of organic chemistry. 2,6-Dichloro phenol showed up as a previously overlooked chemical with the most intense taste and odor. The principal sources of taste and odor are, in order of importance: (1) 2,6-dichloro phenol, (2) 2-chloro-phenol and (3) 2,4-dichloro phenol. The latter chemical was not perceived in low concentration by one panel member. The geometric mean concentration of these chemicals detectable in distilled water was found to be as follows:

Chemical	Geometric Mean Concentrate at Threshold
2,6-Dichloro phenol	2 P.P.B.
2 -Chloro phenol	4 P.P.B.
2,4-Dichloro phenol	8 P.P.B.

At low pH, rates of chlorination of phenol are very low. The previous multiplicity of observations,(7), (8) that application of ammonia prior to chlorination was capable of eliminating or markedly reducing chlorophenolic tastes was further explored. Further evidence of the soundness of this observation was obtained, and in some circumstances, periods of two days and upwards were noted before intense tastes and odors developed, although mild taste and odor could be observed earlier.

The complex interrelationship covering the development of tastes when chlorine is added to systems containing both ammonia and phenols certainly has not been fully studied. The writer takes some satisfaction from the knowledge that further study of the kinetics of phenol chlorination is planned by J. Carrell Morris at Harvard University.

Some Study of the Beaver Falls Experiment

Mr. Kinney's detailed report of the Beaver Falls phenol slug experiment has been available to me. Study of Mr. Kinney's data does not lead me to the same conclusions that Mr. Kinney reaches.

As a frame of reference we might examine some of the data obtained at Chanute, Kansas during the desperate period between October 14, 1956 and March 14, 1957 when that town was obliged to augment its water supply by recirculation of its treated and lagooned sewage as a principal source of raw water. It is estimated that the water was reused about ten times(9). The odor of the raw and finished water was observed thirteen times at

the water plant during the period between January 12 and March 19 by an observer we know to have somewhat better than average odor perception. The median threshold odor of the raw water was 4 with a maximum of 16. With huge quantities of ammonia present in the raw water, plant chlorine feeder capacity forced use of chloramine treatment. Other special measures for taste and odor control were not applied. The finished water was reported to have somewhat poorer odor quality than the raw water, with a maximum threshold odor of 16 and a median threshold odor of 8. Minimum threshold odor on both raw and finished water was 2.

Let us turn now to Beaver Falls, Pennsylvania during the period from February 21 to March 6, 1957 in which Mr. Kinney was attempting to demonstrate that phenolic discharges are not an element of water quality. Mr. Kinney presents the threshold odor of the raw water as follows;- threshold odor 250, 19 times; threshold odor 125, 2 times. The threshold odor of finished water was 25, 4 times at the start moving next to 50 which was the reading with the exception of one T. O. of 83 on February 28. While it is possible to argue about the dominant characteristic of the odor, no one could put up much of a case for the water being potable. If slugs caused the water qualities noted they must have been continuous, and Mr. Kinney has made further comment here that there were none.

The river did an obviously heroic job of assimilating phenols during the period of observation considered and this same heroic self-purification capacity must have worked equally well on sewage pollution. It is difficult for me to see how taste and odor of the magnitude reported could have resulted from any source other than industrial discharges, especially after referring to the Chanute data.

The situation considered appears to be ill-chosen if it is desired to determine whether phenols alone are a significant contributor to taste and odor problems in water supplies. Mr. Kinney's data describe a highly unsatisfactory water during the entire period of maximum phenol discharges to the river. The fraction of the odor distress noted directly attributable to phenol is a matter for conjecture.

When a situation in which finished water with median threshold odor of 50 is offered as proof that phenolic pollution is innocuous, there are no grounds for me to consider further details of the thesis presented.

BIBLIOGRAPHY

1. Manual of Septic Tank Practice. Public Health Service Publication 526.

2. Ettinger, M. B., and Rosen, A. A., "Tastes and Odors in Water." Industrial Wastes, July-August (1958).

3. Ettinger, M. B., and Middleton, F. M., "Plant Facilities and Human Factors in Taste and Odor Control." Jour. A.W.W.A., 48, 1265-73 (1956).

4. Ettinger, M. B., and Auchhoft, C. C., "Removal of Phenol and Cresols from Natural Waters." Ind. Eng. Chem., 41, 1422-7 (1949).

5. Congress (78th) first session, House Document 266, Vol. 2, page 419 (Report of the Ohio River Committee).

6. Burttschell, R. H., Rosen, A. A., Middleton, F. M., and Ettinger, M. B., "The Origin of Chlorophenolic Tastes in Water." Presented before the Division of Water Sewage and Sanitation, American Chemical Society, Los Angeles, California, April 1958.

7. Committee Report "Chlorine-Ammonia Treatment of Water." Jour. A.W.W.A., 33, 2079-2123 (1941).

8. Hassler, W. W., "The History of Taste and Odor Control." Jour. A.W.W.A., 33, 2124-2152 (1941).

9. Metzler, Dwight F., Culp, Russel L., Staltenburg, Howard A., Woodward, Richard L., Walton, Graham, Chang, Shih Lu, Clarke, Norman A., Palmer, Charles M., and Middleton, F. M., "Emergency Use of Reclaimed Water for Potable Supply at Chanute, Kansas." In press, Jour. A.W.W.A. (Scheduled for August 1958).